

## Ambient Levels of Carbonyls in Mexico City

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### RESUMEN

Se determinaron carbonilos ambientales en un sitio de la ciudad de México localizado en el campus de la Universidad Nacional Autónoma de México. Los muestreos se realizaron en la temporada de secas (noviembre y diciembre de 1993, marzo de 1994 y 1995 y febrero de 1996) y en la temporada de lluvias (junio y septiembre de 1995 y mayo, junio, julio y septiembre de 1996). En general, el formaldehído fue el carbonilo que tuvo mayor concentración promedio horaria de 7 a 31 ppbv. Sin embargo, en mayo de 1996 la concentración promedio horaria de acetaldehído estuvo por arriba de 65 ppbv, concentración mucho más alta que la obtenida en todo el periodo de estudio. En junio de 1996, estos niveles disminuyeron a 20 ppbv, que es mayor que el nivel observado en todo el periodo de estudio, con excepción de febrero de 1996 con 22.5 ppbv. No se encontró una explicación satisfactoria sobre los altos niveles de acetaldehído observados en febrero, mayo y a principios de junio de 1996. La acetona, en todo el periodo de muestreo tuvo un promedio horario de 4 a 28 ppbv, siendo ligeramente más alta que o igual a la de formaldehído y acetaldehído en algunos días. Los niveles de propionaldehído (1 a 9 ppbv) y de butiraldehído (1 a 4 ppbv) fueron bajos pero significativos. En general, se observó una disminución de las concentraciones de carbonilos durante la tarde. La comparación de los niveles de carbonilos entre marzo de 1994 y 1995, junio de 1995 y 1996 y septiembre de 1995 y 1996, indicó diferencias significativas ( $p \leq 0.05$ ) sólo entre junio de 1995 y junio de 1996, para el acetaldehído, acetona y propionaldehído. Por otra parte, la concentración de formaldehído (14.9 ppbv) fue más alta en la temporada de lluvias. Las concentraciones de acetaldehído, acetona, propionaldehído y butiraldehído fueron más altas en la temporada de secas (14.1, 12.4, 2.5 y 2.3 ppbv, respectivamente).

### ABSTRACT

Measurements of ambient carbonyls were carried out at one sampling site at the University of Mexico campus, Mexico City in dry season (November and December 1993, March 1994, and February and March 1996), and rainy season (June and September 1995, May, June, July, and September 1996). In general, formaldehyde had higher average hourly concentrations than those of the other sampled carbonyls, however, in May 1996, acetaldehyde concentrations were above 65 ppbv; much higher than the obtained for all the period of study. In June 1996, these levels decreased to 20 ppbv, even higher than the observed values in all the period of study, except February 1996 with 22.5 ppbv. It was not found a satisfactory explanation for the acetaldehyde levels observed in February, May and at the beginning of June 1996. Average hourly concentrations of acetone from 4 to 28 ppbv for all the period study were slightly higher or equal to formaldehyde and acetaldehyde concentrations at some days. Propionaldehyde (1 to 9 ppbv) and butyraldehyde (1 to 4 ppbv) levels were small but significant. In general, a decrease in carbonyl concentrations during the evening was observed. Comparison of carbonyl concentrations between March 1994 and 1995, June 1995 and June 1996 and September 1995 and 1996, indicated a significant difference ( $p \leq 0.05$ ) for acetaldehyde, acetone and propionaldehyde. On the other hand, formaldehyde concentration (14.9 ppbv) was higher in rainy season and acetaldehyde, acetone and butyraldehyde were higher in dry season (14.1, 12.4, 2.5 y 2.3 ppbv, respectively).

## 1. Introduction

There are many documented literature descriptions of the chemical and toxicological characteristics of ambient carbonyl compounds. Primarily, formaldehyde and acetaldehyde are of critical importance as components of photochemical pollution, products of the photo-oxidation of gas-phase hydrocarbons, major source of free radicals and as precursors to organic-aerosol formation in urban air (Grosjean, 1988; Carlier *et al.*, 1986; Dodge, 1990; Anderson *et al.*, 1996).

Previous studies on ambient aldehydes levels in urban, rural and maritime atmospheres have been published (Thompson, 1980; Zafiriou *et al.*, 1980; Salas and Singh, 1986; Grosjean, 1988; Kalabokas *et al.*, 1988; Tanner *et al.*, 1988; Báez *et al.*, 1989; Grosjean *et al.*, 1990; Gunz and Hoffmann, 1990; Shepson *et al.*, 1991; Grosjean *et al.*, 1993). The main concern for researchers are the high levels of formaldehyde and acetaldehyde reported in polluted atmospheres such as Los Angeles, CA; Paris; Sao Paulo and Rio of Janeiro, Brazil; Budapest, Hungary; Atlanta, Georgia; and Mexico City (Grosjean and Fung, 1984; Kalabokas *et al.*, 1988; Grosjean *et al.*, 1990; Haszpra *et al.*, 1991; Grosjean *et al.*, 1993; Báez *et al.*, 1995).

The increased use of oxygenated fuel with addition of methyl-t-butyl-ether (MTBE) produced a substantial increase of aldehydes, in particular formaldehyde and acetaldehyde (Anderson *et al.*, 1996). This fuel is being used in Mexico City. It was considered necessary to carry out measurements of ambient carbonyls due to the high levels of ozone and other pollutants in the atmosphere of Mexico City. Formaldehyde and acetaldehyde were measured at different periods from 1993 to 1996 and acetone, propionaldehyde and butyraldehyde from 1995 to 1996.

## 2. Experimental

### 2.1 Sampling

Samples were collected at 2 hours intervals on the roof of the Atmospheric Sciences Research Building located at the University of Mexico campus, 15 km south of Mexico City downtown from 800 to 1800 h. The sampling was done from 1993 to 1996 in different months of the dry and rainy seasons. In the dry season: November and December 1993, February 1996, and March 1994 and 1995. In the rainy season: June and September 1995, May, June, July, and September 1996.

Great variations in smog conditions are observed in the Mexico City Metropolitan Zone attributable to the prevailing meteorological conditions. Temperature inversions and stagnation conditions prevail almost daily from November to March. Thunderstorm activity is frequent from June to September when trade winds are well established. Formaldehyde, acetaldehyde, acetone, propionaldehyde and butyraldehyde were measured. In 1993 and 1994 carbonyls with higher molecular weight (acetone, propionaldehyde and butyraldehyde) were not detected. Sampling in 1993-1994 was done by using two microimpingers connected in series containing 20 mL of an acidified solution of 2,4-dinitrophenylhydrazine (DNHP) in acetonitrile cooled in an ice bath (Kalabokas *et al.*, 1988). Air was bubbled at a rate of 0.75-L min<sup>-1</sup>. Although this sampling technique is relatively simple and economical, it is cumbersome for field studies requiring large numbers of samples and for those conducted at remote sites (Shepson *et al.*, 1991). Since 1995 sampling was done with Sep-Pak DNPH-Silica cartridges (Waters Corp.), which are easily handled in fieldwork, besides, slightly higher sampling flow rates are possible (Shepson *et al.*, 1991). With this technique air was passed through of cartridges at a rate of 1-L min<sup>-1</sup>. An ozone scrubber was placed upstream the cartridge to avoid degradation of hydrazone derivatives (Waters, 1994). The formed 2,4-dinitrophenylhydrazones were eluted with 10 mL of acetonitrile.

## 2.2 Analysis

Twenty- $\mu\text{L}$  sample aliquots were injected and analyzed by high performance liquid chromatography (HPLC) with ultraviolet detection at a wavelength of 360 nm. The instrument used was a Perkin-Elmer equipped with an isocratic LC Pump Model 250 and an Epson P. C. computer, a Spherisorb S5 ODS2 reverse phase analytical column and a GBC LC 1200 UV/VIS detector. The mobile phase was 55% acetonitrile/45% water at  $1\text{-mL min}^{-1}$ . Calibration was done by direct injection of standard mixtures with known amounts of solid hydrazone derivatives dissolved in HPLC-grade acetonitrile.

Cartridge laboratory blanks were run to determine background levels of DNPH derivatives.

The average blank values of 5 different lots were  $0.47 \pm 0.31$  (SD),  $0.39 \pm 0.12$  and  $0.92 \pm 0.48$   $\mu\text{g}/\text{cartridge}$  for formaldehyde, acetaldehyde and acetone, respectively. Propionaldehyde and butyraldehyde were not detected. Ambient carbonyl levels were corrected for cartridge field blanks.

## 2.3 Detection limits, precision and collection efficiencies

The limits of detection for sampling with microimpingers for formaldehyde and acetaldehyde were 0.4 and 0.97 ppbv, respectively, for a sample of 120 liters corresponding to the sampling conditions (Báez *et al.*, 1995). For Sep-Pak DNPH-Silica cartridges, analytical detection limits for formaldehyde, acetaldehyde, acetone, propionaldehyde and butyraldehyde derivatives were 0.043, 0.033, 0.044, 0.009 and  $0.015 \mu\text{g mL}^{-1}$ , respectively (mean values from 5 determinations), according to the method described by Miller and Miller (1993). These detection limits correspond to 0.54, 0.56, 0.94, 0.2 and 0.33 ppbv for formaldehyde, acetaldehyde, acetone, propionaldehyde and butyraldehyde, respectively, for a sample volume of 120 L, corresponding to the sampling conditions.

The precision of the method was evaluated from data obtained from four co-located samplers. The results for the impingers were 6.7% and 10.7% RSD for formaldehyde and acetaldehyde, respectively, and for the cartridges, ranged from 0.30 to 12.14% RSD for all the carbonyls.

Impinger collection efficiencies for formaldehyde and acetaldehyde were 88% and 86%, respectively (Báez *et al.*, 1995). Cartridge collection efficiency was determined with two cartridges connected in series, values were  $>95\%$  for all carbonyls.

## 3. Results and discussion

Thirteen samples were collected in November and 14 in December 1993 corresponding to 3 sampling days in each month, 55 in March 1994 (11 sampling days), 20 in June and 24 in September 1995 (5 sampling days in each month). In 1996, 14 in February (3 sampling days), 10 in March (2 sampling days), 31 in May (7 sampling days), 31 in June (7 sampling days), 18 in July and 11 in September (4 and 2 sampling days, respectively).

In November 1993, average hourly variations (Fig. 1a) were similar for both aldehydes with a decreasing towards the afternoon and maximum values of 31 and 29 ppbv from 800 to 1000 h for formaldehyde and acetaldehyde, respectively. However, acetaldehyde concentrations (10.9 ppbv) were slightly higher from 1400 to 1800 h.

Figure 1b shows the average hourly concentrations corresponding to December 1993. Very little variations are observed for both aldehydes with time of day. Formaldehyde had a maximum

concentration (26 ppbv) from 1000 to 1200 h and acetaldehyde (24 ppbv) from 1400 to 1600 h. Acetaldehyde concentrations were slightly higher than formaldehyde concentrations from 1400 to 1800 h.

Figure 1c shows that in March 1994 average hourly variations were small with maximum concentrations for both aldehydes (18.3 and 13.9 ppbv for formaldehyde and acetaldehyde, respectively) from 1000 to 1200 h. Minimum concentrations of 9.6 and 6.5 ppbv for formaldehyde and acetaldehyde, respectively, were observed from 1600 to 1800 h.

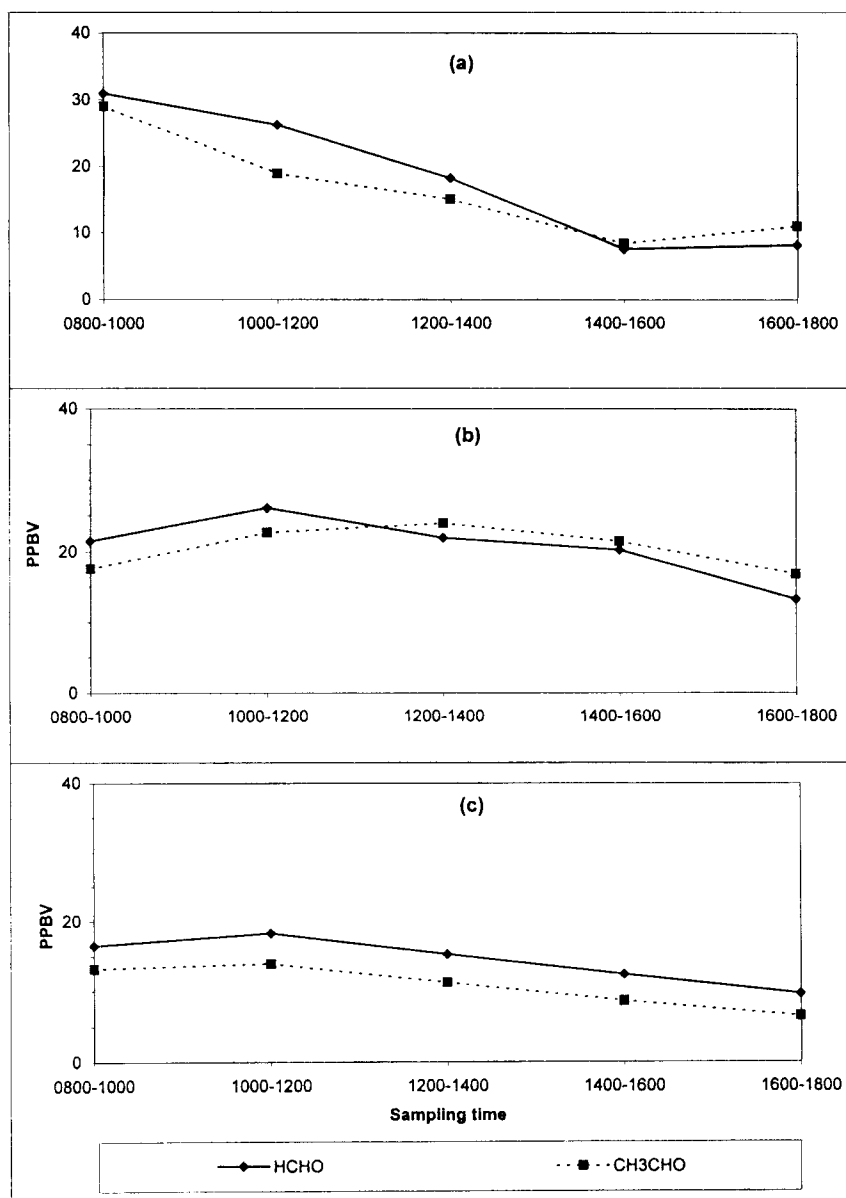


Fig. 1. Formaldehyde and acetaldehyde mean concentration variation in function of time of day for (a) November 1993, (b) December 1993, (c) and March 1994.

Figures 2a and 2b show the average hourly variations for June and September 1995, respectively. Carbonyl concentrations reached their average maximum values between 1200 and 1400 h. In June, these concentrations were 15, 11.4, 10.7, 2.2 and 3.1 ppbv for formaldehyde, acetaldehyde, acetone, propionaldehyde and butyraldehyde, respectively. In September, the concentrations were 27, 17, 14, 3.5 and 4 ppbv for the same carbonyls. This variation pattern suggests that photochemical reactions are important contributors to the carbonyls measured during these months.

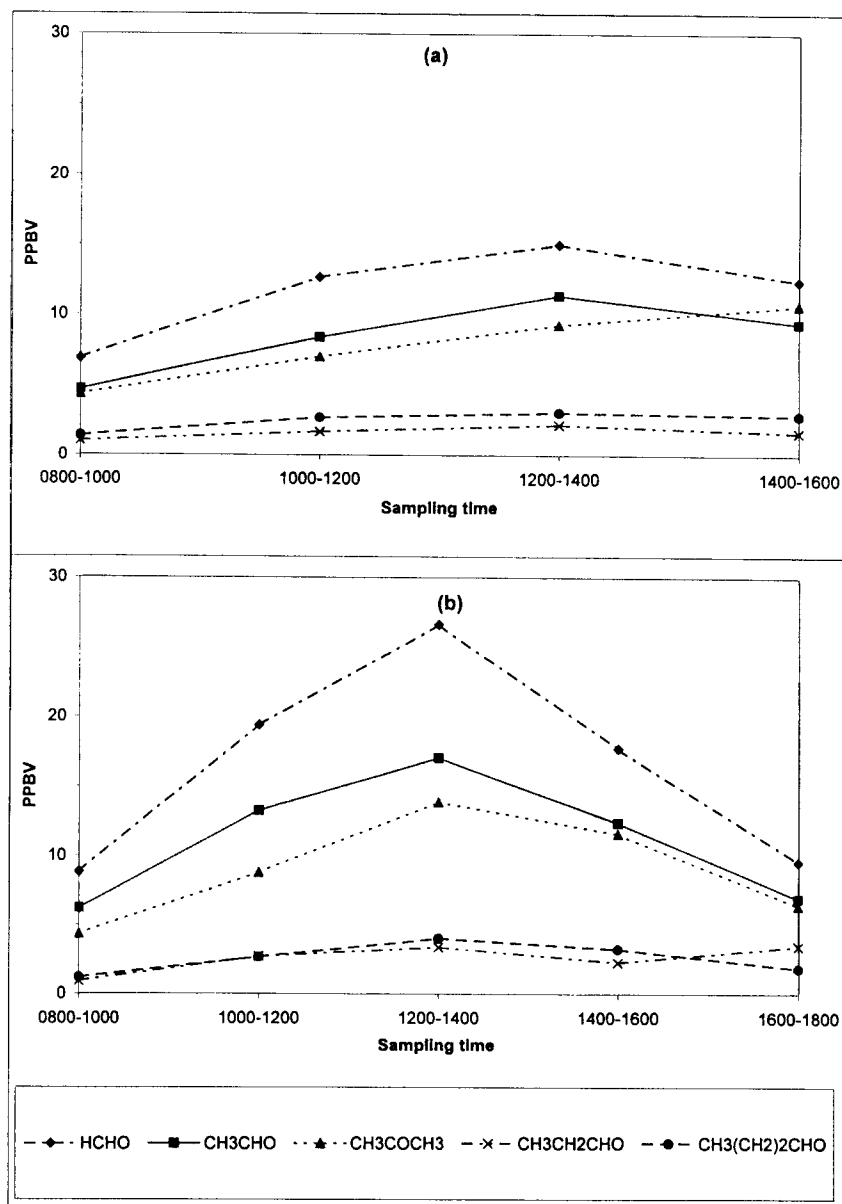


Fig. 2. Carbonyls mean concentration variations in function of time of day for (a) June 1995 and (b) September 1995.

Figure 3 shows the hourly average carbonyl concentrations corresponding to February, March, May, June, July, and September 1996. In February (Fig. 3a), the maximum concentrations occurred from 1000 to 1200 h for all the carbonyls, being acetaldehyde the carbonyl with the highest concentration (22 ppbv), followed in order by acetone and formaldehyde with 20 and 14 ppbv, respectively. It is important to mention that acetone concentrations were a little higher than those of acetaldehyde at some hours of the day. In March, July, and September (Figs. 3b, 3e, and 3f), the average concentrations of formaldehyde were 18, 26 and 22 ppbv, respectively, being higher than those of the acetaldehyde 17, 16 and 14 ppbv, and acetone, 6, 13 and 13 ppbv. Maximum carbonyl concentrations were observed from 1000 to 1200 in March and from 1200 to 1400 h in July and September, except acetaldehyde, whose maximum concentrations were observed from 800 to 1000 in March and from 1000 to 1200 in September. On the other hand, the average concentrations of propionaldehyde and butyraldehyde ranged from 1.1 to 3.2 ppbv and 0.9 to 4.1 ppbv, respectively, with little variations through the sampling hours with maximum levels between 1000 and 1400 h.

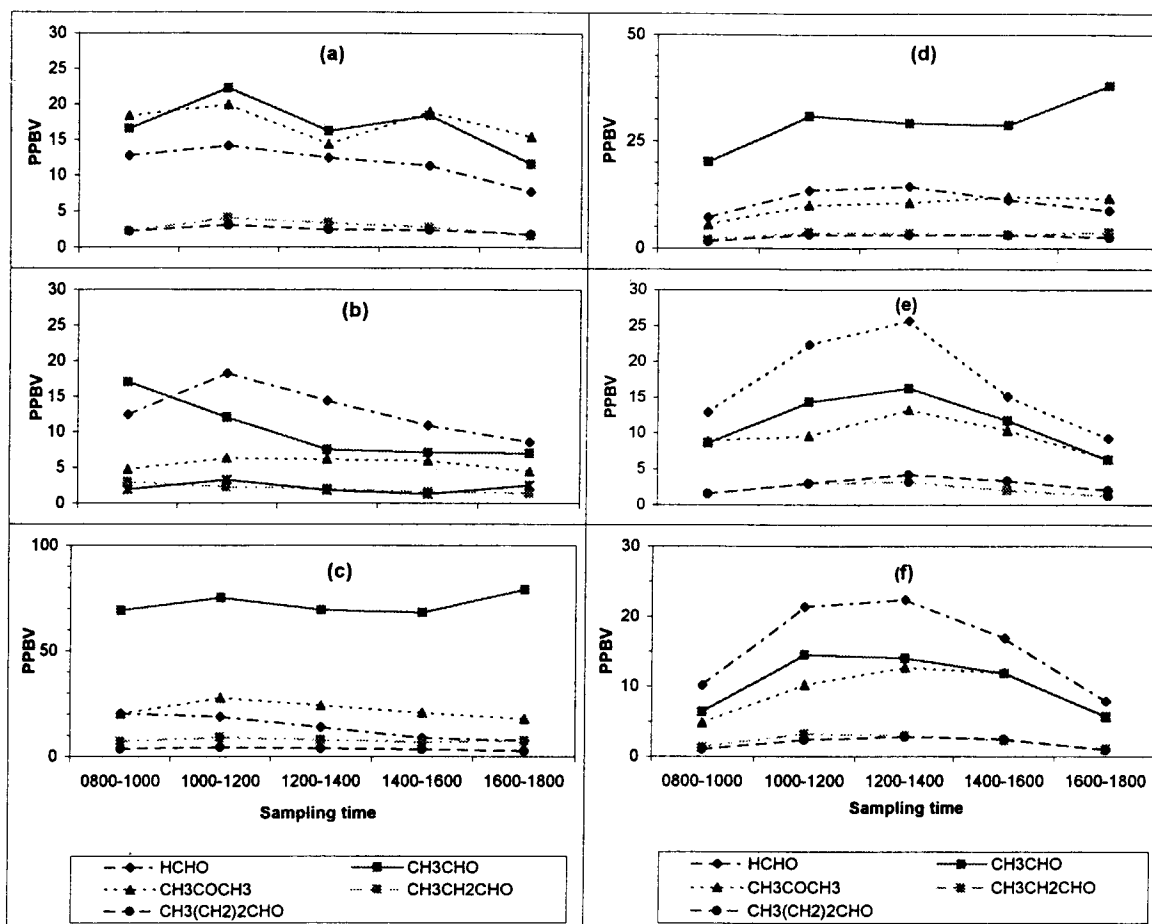


Fig. 3. Same as Figure 2, except for (a) February 1996, (b) March 1996, (c) May 1996, (d) June 1996, (e) July 1996, and (f) September 1996.

In May and June 1996 (Figs. 3c and 3d), average hourly acetaldehyde concentrations were much higher than those observed during the rest of the sampling months. In May, the concentrations were above 65 ppbv with a maximum of 79 ppbv from 1600 to 1800 h., and in June, a maximum concentration of 38 ppbv was observed in the same hours with a minimum of 20 ppbv from 800 to 1000 h. Concerning formaldehyde, maximum concentrations were of 20 and 14 ppbv

from 800 to 1000 h and 1200 to 1400 h. for May and June, respectively. Acetone concentrations were higher in May than in June with a maximum of 28 and 12 ppbv from 1000 to 1200 h and 1400 to 1600 h, respectively. Propionaldehyde and butyraldehyde presented little variations with maximum values of 9 and 4 ppbv, respectively, from 1000 to 1200 h. In general, a decrease in the concentration of all the carbonyls through the evening was observed.

Table 1 shows monthly average, minimum and maximum carbonyl concentrations corresponding to all sampling period. In December 1993, formaldehyde had the highest average concentration with 21.1 ppbv. This result is expected, since in this month high pollution levels and stagnation conditions are present in the atmosphere of Mexico City. However, in September 1995 and July 1996, formaldehyde concentrations (16.8 and 17.7 ppbv) were as high as in November 1993 (16.6 ppbv).

Table 1. Minimum, maximum, and average carbonyl concentrations measured in some months of 1993, 1994, 1995 and 1996.

| Statistic            | Nov 93 | Dec 93 | Mar 94 | Jun 95 | Sep 95 | Feb 96 | Mar 96 | May 96 | Jun 96 | Jul 96 | Sep 96 |
|----------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| <b>Formaldehyde</b>  |        |        |        |        |        |        |        |        |        |        |        |
| Average              | 16.6   | 21.1   | 14.4   | 11.8   | 16.8   | 11.6   | 12.9   | 13.8   | 11.4   | 17.7   | 14.9   |
| Minimum              | 6      | 10.6   | 5.9    | 3.1    | 5.2    | 6.4    | 5.7    | 5.4    | 3.8    | 7.7    | 7.2    |
| Maximum              | 34.8   | 40     | 24.7   | 22     | 36     | 18.6   | 18.3   | 29     | 22     | 32.4   | 26.7   |
| <b>Acetaldehyde</b>  |        |        |        |        |        |        |        |        |        |        |        |
| Average              | 15.3   | 20.7   | 10.7   | 8.5    | 11.4   | 17     | 10.1   | 71.8   | 29.4   | 11.8   | 9.9    |
| Minimum              | 2      | 9      | 0.6    | 2.8    | 3.4    | 3.3    | 5.2    | 44.2   | 4      | 5.1    | 4.3    |
| Maximum              | 37.8   | 41.2   | 23.8   | 16.2   | 23.4   | 29.4   | 18.9   | 98.8   | 84.8   | 19.6   | 19.6   |
| <b>Acetone</b>       |        |        |        |        |        |        |        |        |        |        |        |
| Average              | ---    | ---    | ---    | 7.9    | 9.1    | 17.3   | 5.5    | 22.4   | 10.1   | 9.9    | 8.6    |
|                      | ---    | ---    | ---    | 2.1    | 2.6    | 4      | 2.5    | 11.2   | 2.7    | 4.2    | 3.4    |
|                      | ---    | ---    | ---    | 19.4   | 16.3   | 34.3   | 9.7    | 77.4   | 20.2   | 16.6   | 14.9   |
| Average              | ---    | ---    | ---    | 1.7    | 2.5    | 2.8    | 2      | 7.6    | 3.2    | 2.2    | 2.1    |
| Minimum              | ---    | ---    | ---    | ND     | ND     | 0.7    | ND     | 5      | ND     | 0.8    | 1      |
| Maximum              | ---    | ---    | ---    | 3.4    | 10.5   | 5      | 4.5    | 11.2   | 7.8    | 4.4    | 4.3    |
| <b>Butyraldehyde</b> |        |        |        |        |        |        |        |        |        |        |        |
| Average              | ---    | ---    | ---    | 2.5    | 2.6    | 2.4    | 2.1    | 3.5    | 2.7    | 2.9    | 1.8    |
| Minimum              | ---    | ---    | ---    | ND     | ND     | 0.9    | 6      | 1.9    | ND     | ND     | 0.6    |
| Maximum              | ---    | ---    | ---    | 4.4    | 5      | 3.5    | 4.2    | 8.4    | 4.5    | 5.2    | 3.2    |

In May and June 1996, monthly average acetaldehyde concentrations (71.8 and 29.4 ppbv) and maximum acetaldehyde concentrations (98.8 ppbv and 84.8 ppbv) were higher than those observed in the other sampling months. Also, they were higher than those of formaldehyde (13.8 and 11.4 ppbv) and acetone (22.4 and 10.1 ppbv) in these months. Acetone, shows little variation, with the highest concentrations in February and May 1996 (17.3 and 22.4 ppbv). Concerning propionaldehyde and butyraldehyde, their concentrations presented little differences in all sampling months, except in May when propionaldehyde had the highest monthly average concentration (7.6 ppbv).

The most important sources of formaldehyde and acetaldehyde in the atmosphere are direct emissions from motor vehicles (Anderson *et al.*, 1996) and secondary reactions of alkanes and

alkenes (Altshuller, 1993). For example, the reaction of trans-2-butene with OH and NO<sub>x</sub> which produces 92% of acetaldehyde from the formed alkoxyradicals and also 92% of acetaldehyde from the reaction of the radical CH<sub>2</sub>CHOH with O<sub>2</sub> (Finlayson-Pitts and Pitts, 1986).

Secondary reactions, undoubtedly, contribute substantially to the levels of formaldehyde and acetaldehyde found in the Mexico City atmosphere, however, they do not explain the high acetaldehyde concentrations measured in May and June 1996, which in fact were higher than those of formaldehyde. If these sources had been the only contributions of acetaldehyde, the high concentrations observed in May and June would have also been observed in the remaining months, regardless the meteorological conditions that affect carbonyl levels.

Next, are summarized some reasons that could explain an increase of acetaldehyde concentrations observed in May and June 1996. Forest fires are another source of aldehydes, they occur mainly during the dry months, March, April and May. The forests located to the south and southwest of Mexico City have complex tree populations, i.e. caduceus and coniferous species. These forests lie not farther than 40 km from the sampling site and are usually exposed to wild-fires that last several days and also weeks during the mentioned months every year. It has been reported that wood burning and forest fires are important sources of aldehydes (Lipari *et al.*, 1984; Carlier *et al.*, 1986). In wood-burning study tests in fireplaces, formaldehyde, acetaldehyde and p-tolualdehyde were the major aldehydes emitted, that ranged from 21 to 42%, 7-14% and 10-26% of the total aldehyde emissions, respectively (Lipari *et al.*, 1984). However, forest fires do not seem to explain the fact that acetaldehyde concentrations were higher than those of formaldehyde.

On the other hand, the overall photolytic lifetime ( $\tau$ ) of formaldehyde and acetaldehyde at different hours and months at 19°20'N latitude (Mexico City) were estimated (Báez *et al.*, 1999). For formaldehyde,  $\tau$  ranged from 3.2 to 10.5 hours, the smallest values corresponded to hours with high actinic flux between 1100 to 1600 h, solar time. For acetaldehyde, the range of  $\tau$  was from 56 to 102 hours, as it was expected, again the lower values corresponded to the high actinic flux at noon hours. The faster formaldehyde photolysis rate and the transport time fire fumes take to arrive to the sampling site, could help to explain why acetaldehyde concentrations were higher than those of formaldehyde in May and June 1996.

The CH<sub>3</sub>CHO/CH<sub>2</sub>O ratio has changed through the different years. This ratio was 0.92 and 0.98 in November and December 1993, 0.74 for March 1994, 0.72 and 0.68 for June and September 1995, and 1.47, 0.79, 5.21, 2.58, 0.67 and 0.67 for February, March, May, June, July and September 1996, respectively. Acetaldehyde concentrations were high in February, May and June 1996, as it was mentioned before. However, it is interesting to remark that acetaldehyde concentrations were high only from June 1 to 4, 1996 (77 ppbv, not shown in Fig. 3d). Acetaldehyde concentrations did not vary significantly during the rest of the sampling period.

The reasoning exposed in the previous paragraphs clearly shows that there is not a satisfactory explanation to account for both the high acetaldehyde concentrations and acetaldehyde/formaldehyde ratio values (1.47, 5.21 and 2.58).

As a further information, five percent of methyl-t-butyl-ether (MTBE) was added to gasoline in November 1989 to reduce carbon monoxide and hydrocarbons emission (GDF, 1998). According to Andersson *et al.* (1996), the MTBE increases by comparable amounts the emissions of formaldehyde and acetaldehyde. Clearly, the addition of MTBE does not explain the high acetaldehyde concentrations.

Regarding acetone, Chatfield *et al.* (1987) explained that it is formed in the troposphere by the attack of HO radical upon certain alkanes and alkenes. Also, acetone is formed by the reaction of ozone with some alkenes and it is the major ultimate product of HO radical oxidation of



propanone, isobutane, isopentane and higher isoalkanes (Chatfield *et al.*, 1987). From the above discussion it may be suggested that photochemical reactions are an important source of acetone in the atmosphere of Mexico City. Possibly, the oxidation of propane is the main photochemical reaction since, approximately more than 90% of houses, hotels, restaurants, bakeries and many small industries use liquefied petroleum gas, for cooking, water heating, etc., in Mexico City metropolitan area. Liquefied gas is sold in small portable cylinders for domestic use with 20 to 30 kg of fuel content, which are manually changed as soon as they are emptied, emitting large quantities of propane and butane. In big department buildings, hotels and small industries, the fuel is contained in bigger tanks (300kg and up) which are refueled by tank trucks without vapor recovery systems, also emitting propane and butane to the atmosphere. There are other potential sources of acetone, like the chemical industry that uses acetone in its processes and the use of solvents containing acetone. All these facts seem to explain the present levels of this carbonyl observed in the atmosphere of Mexico City.

With respect to propionaldehyde and butyraldehyde they were only present in small concentrations. Propionaldehyde is associated with anthropogenic hydrocarbons.

Comparison of average concentrations was applied only for the months of March 1994 and 1996, June 1995 and 1996, and September 1995 and 1996. It is observed that a small decrease in the concentration of formaldehyde occurred from 14.4 to 12.9 ppbv in March, from 11.8 to 11.4 ppbv in June and from 16.8 to 14.9 ppbv in September. This was also observed for acetaldehyde from 10.7 to 10.1 ppbv in March and from 11.4 to 9.9 ppbv in September. On the contrary, an increase from 8.5 to 29.4 ppbv was observed in June. Acetone, propionaldehyde and butyraldehyde show an increase in June and a decrease in September. The Wilcoxon-Mann-Whitney two-tailed test indicates a significant difference ( $p \leq 0.05$ ) for acetaldehyde, acetone and propionaldehyde concentrations ( $Z$  values of 2.90, 1.98 and 2.12, respectively) between June 1995 and June 1996.

It was only compared average concentrations in the dry months February and March 1996 with those in the rainy months July and September 1996. Formaldehyde concentrations were higher in the rainy season (14.9 ppbv) than in the dry season (12.1 ppbv). Acetaldehyde, acetone, propionaldehyde and butyraldehyde concentrations were higher in the dry season (14.1, 12.4, 2.5 and 2.3 ppbv, respectively) than in the rainy season (9.9, 8.6, 2.1 and 1.8 ppbv, respectively). It was not possible to explain the differences between these seasons. February and March are characterized by strong winds that disperse air pollutants, however, the rains during July and September also scavenged the pollutants.

#### 4. Conclusions

In general, formaldehyde had the highest average hourly and monthly concentrations, ranging from 7 to 31 and 11.4 to 21.1 ppbv, respectively. However, acetaldehyde had higher concentration than formaldehyde in February, May and June 1996, mainly in these last two months when unexplained high acetaldehyde concentrations were measured. That is, the highest acetaldehyde concentrations were 98.8 ppbv in May and 84.8 ppbv in June, with average monthly concentrations for the same months of 71.8 and 29.4 ppbv, respectively.

The most important result was the fact that acetaldehyde to formaldehyde ratios were as high as 5.21 in May 1996, even though ethanol is not used as fuel in vehicles in Mexico City. Forest fires in combination with the overall photolytic lifetime of formaldehyde and acetaldehyde could help to explain why acetaldehyde concentration was higher than that of formaldehyde in February, May and June 1996. The acetaldehyde to formaldehyde ratio has been changing throughout the sampling years.

The comparison of the average concentrations of carbonyls between the months of March 1994 and 1996, June 1995 and 1996, and September 1995 and 1996 indicated a small decrease in the concentration of formaldehyde. Also, acetaldehyde decreased with the exception of June, month in which an increase of this aldehyde was observed, but it was due to the unexplained high values that were measured in May and June of 1996.

The Wilcoxon-Mann-Whitney two-tailed test applied indicated only a significant difference between March 1994 and 1995, June 1995 and June 1996 and September 1995 and 1996, for acetaldehyde, acetone and propionaldehyde. It is important to mention that these statistical tests were applied to relatively small groups of data.

Formaldehyde concentration (14.9 ppbv) was higher in rainy season and acetaldehyde, acetone and butyraldehyde were higher in dry season (14.1, 12.4, 2.5 y 2.3 ppbv, respectively). Then it is recommended a more intensive and continuous sampling during the different seasons to understand better the photochemical behavior of carbonyls in function of emission factors and meteorological parameters.

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